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MIGRATION OF HARMFUL SUBSTANCES FROM COLORED GLAZES INTO MODEL MEDIA

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The results of investigations of colored glazes containing oxide colorants (Cr_2O_3 , CuO , CoO , Mn_2O_3), added to the batch when colored frit is being melted and when the transparent glaze frit is ground, are presented. It is established that these oxides affect the LTEC, the microhardness of the glazes, and the migration of boron, aluminum, chromium, copper, cobalt, and manganese ions out of the coatings into a 4% solution of acetic acid. The relation between the structural changes occurring in colored glassy coatings and the migration of harmful substances out of them is determined.

One way food becomes contaminated with harmful substances is migration from glazed ceramic dishware while it is in contact with the food.

Hygienic norms for the content of the most dangerous elements have now been developed for food products. For example, according to SanPiN 13-3 RB 01, the admissible amounts of migration from glazed ceramic dishware cannot exceed 0.1 mg/liter for cobalt, chromium, and manganese, 1.0 mg/liter for copper, 4.0 mg/liter for boron, and 0.5 mg/liter for aluminum. Any amounts of these elements above these levels can have serious health consequences.

Boron present in the body in elevated quantities is quickly and almost completely absorbed in the gastrointestinal tract, which becomes irritated. Prolonged exposure to boron compounds leads to boron intoxication, which can damage the liver, kidneys, and central nervous system. Investigations performed by the World Health Organization have determined the maximum daily consumption of boron to be 88 $\mu\text{kg/kg}$ body mass.

In most cases aluminum enters the body from food, containers where aluminum is a constituent element, glazes. Aluminum can block the activity of enzymes which participate in the transmission of impulses to the nervous system, which lowers brain activity and leads to memory loss.

Chromium is encountered in two forms — Cr^{6+} and Cr^{3+} . Hexavalent chromium compounds are the most poisonous ones. They are absorbed in the gastrointestinal tract more easily than the trivalent compounds. Chromium can accumulate in the liver, pancreas, and marrow and it can alter the activity of enzymes. In addition, chromium and some of its

compounds are carcinogenic in man and can act as mutagens [1, 2].

Manganese is one of the trace elements that are biologically necessary for humans. It plays an important role in the formation of connective tissue and bones, body growth, and carbohydrate metabolism. Mn^{2+} and Mn^{3+} ions have a large capacity for complexing in biological media. The bivalent manganese compounds are 2.5 – 3 times more toxic than the trivalent compounds [1, 2].

Cobalt in the human body can be in the oxidation states +2 and +3, of which Co^{3+} is most toxic. There is information that the solubility of cobalt in the acidic and alkaline media of the gastrointestinal tract is good and as a result its absorption is high [2]. The norm for the cobalt content in human blood is 0.1 – 3.9 $\mu\text{kg/liter}$. Cobalt at critical concentration levels induces biochemical changes in and disrupts the functional state of the body.

The biochemical activity of copper is high. As a result, metabolism is seriously disrupted when excess copper enters the body. This is manifested as toxic effects. The safe level of copper ingestion is 1.5 – 3.0 mg/day for adults and 0.4 – 2.5 mg/day for children [1].

The problem of the migration of harmful substances is of interest because glazes, including colored ones, are now widely used in the ceramic industry for decorating items used in the home. However, it should be noted that there are comparatively few publications devoted to sanitary – chemical studies of glazed ceramic dishware. The migration of the harmful substances present simultaneously in glazes has not been adequately studied.

Our objective in the present work is to establish a relation between the structural changes in the aluminoborosili-

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cate network of colored glassy coatings and the migration of harmful ions from them.

In our previous investigations [3], we determined the region of formation of transparent coatings with a low content of B_2O_3 based on high-alumina region of the glass-forming system $Na_2O - K_2O - RO - B_2O_3 - Al_2O_3 - SiO_2$. The experimental data obtained in the studies of the migration of boron and aluminum ions made it possible to determine the optimal compositions. A transparent glaze containing 10.0%² ($Na_2O + K_2O$), 2.0% SrO , 15.8% B_2O_3 , 5.0% Al_2O_3 with SiO_2 making up the remainder was chosen as the initial (optimal) composition used for synthesizing colored glazes. Our studies showed that the concentrations of aluminum and boron ions which leave the transparent coating and enter a 4% solution of acetic acid are, on average, 0.03 and less than 0.5 mg/liter, respectively. This meets falls within the sanitary norms.

The oxide colorants (Cr_2O_3 , CuO , CoO , Mn_2O_3) were added in amounts above 100% into the batch when melting the colored frits and in amounts of 1 and 5, 1 and 8, 1 and 6, and 1 and 8%, respectively, when the transparent glaze frit was ground. These amounts were chosen on the basis of an analysis of the published data and the technical documentation provided by a number of ceramic works.

The compositions of the colored glazes were denoted as follows: A) contains chromium, B) copper, C) manganese, D) cobalt. For example, A1 denotes a composition to which 1% above 100% chromium oxide was added to the batch; A1f — 1% above 100% chromium oxide added to transparent frit during grinding; and, similarly for B, C, and D.

The experimental frits were melted in 0.3 liter porcelain crucibles placed inside a gas-flame furnace at temperatures 1400–1450°C with soaking at the maximum temperature for 1.5 h until a uniform glass mass with no visible batch inclusions was obtained in a filament test.

The glazes were prepared by wet-grinding of colored frits as well as transparent frit to which oxide colorants were added. "Vesko-Keramik" refractory clay was added in an amount equal to 7% above 100% to improve grindability and the rheological characteristics of the glaze slips. The moisture content of the glaze suspension was 40–42%. The glaze was deposited on prefired majolica articles manufactured by Belkhudozhkeramika JSC using local polymineral clays. The glazes deposited by dipping fused at 1000°C in chamber and multichannel electric furnaces at the factory.

The boron, aluminum, and manganese contents were determined by the photometric method following GOST 24295–80, GOST 18165–89, and GOST-4974–72, respectively. The concentrations of chromium, copper, and cobalt ions were determined by inverted voltammetry using an AVA-2 voltammeter.

Structure sensitive properties of the glazes, such as the microhardness, CLTE, and the migration level of harmful

ions normalized to the sanitary norms give information on the structure of the glasses and are of theoretical and practical interest for synthesizing and optimizing the composition of high-quality glazes.

The microhardness of the glazes was determined on a PRM-3M apparatus (LOMO, Russia) with a 1 N load on the indicator. The data were analyzed with a photoelectronic micrometer (Spektr OSB, Russia). The admissible error is $\pm 3\%$.

The experiment established that the microhardness of the glazes which were studied ranges from 5080 to 6840 MPa. Increasing the chromium oxide content from 1 to 5% and copper oxide from 1 to 8% decreases the microhardness from 6550 to 5080 and from 6840 to 6420 MPa, respectively. Conversely, in glazes containing manganese and cobalt oxides, increasing the amount of Mn_2O_3 from 1 to 8% and CoO from 1 to 6% increases the microhardness from 6390 to 6800 and 6250 to 6480 MPa, respectively.

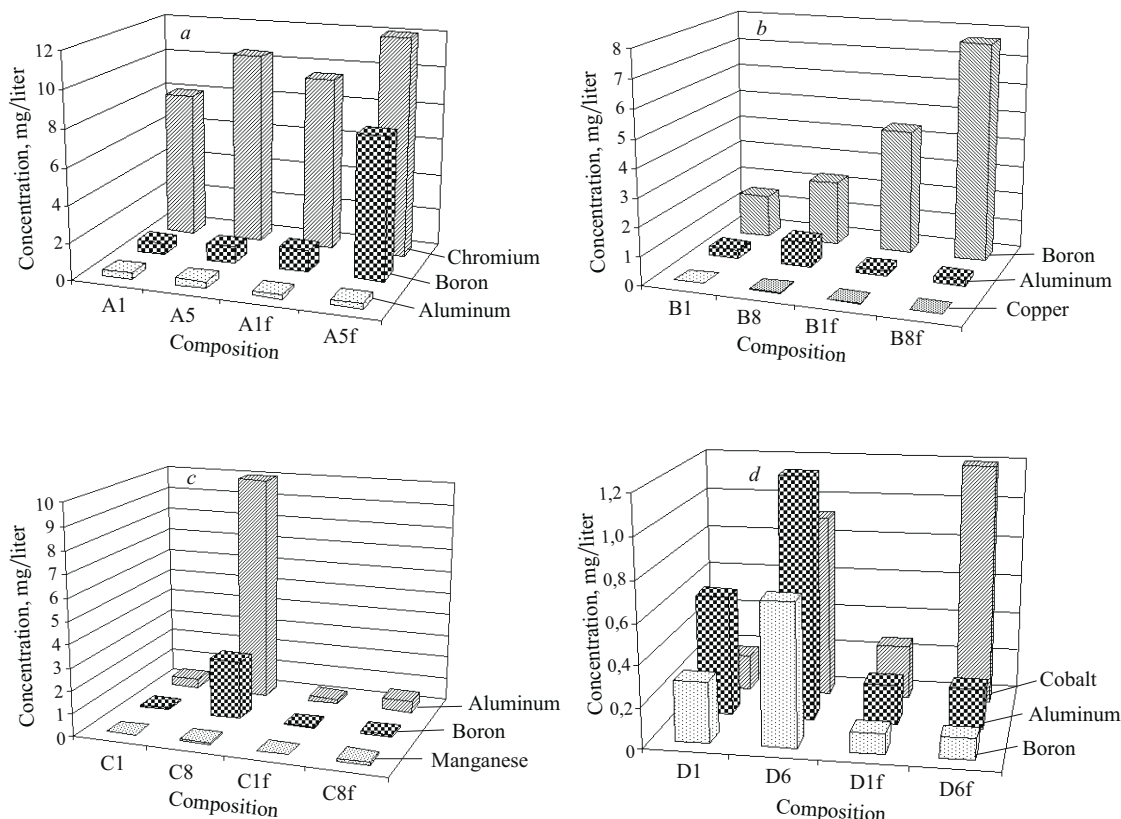
The values of the CLTE determined experimentally on the DIL 402 PC electronic dilatometer, manufactured by the Netzsch Company, in the temperature range 20–400°C are $(52.3 - 74.5) \times 10^{-7} K^{-1}$ for the glazes studied. Increasing the chromium oxide content from 1 to 5% and copper oxide from 1 to 8% increases the CLTE from 61.3×10^{-7} to $74.5 \times 10^{-7} K^{-1}$ and from 57.3×10^{-7} to $61.5 \times 10^{-7} K^{-1}$, respectively. Manganese oxide added in the amounts 1 and 8% and cobalt oxide in the amounts 1 and 6% decrease the CLTE from 59.17×10^{-7} to $52.3 \times 10^{-7} K^{-1}$ and from 62.0×10^{-7} to $60.4 \times 10^{-7} K^{-1}$, respectively.

It is well known that the CLTE and microhardness depend primarily on the strength of the bonds and the interaction force between the structural components and on the packing density. The CLTE increases as the structure of glasses becomes weaker. For compositions containing copper and chromium oxides, the decrease of the microhardness and the increase of the CLTE are due to the decreases of the structural connectivity of the glasses.

As for manganese and cobalt, it is likely that in the glasses studied they can be represented in form of the ions Mn^{2+} , Mn^{4+} , Co^{2+} , and Co^{4+} , and their ratio depends on the conditions of synthesis. On this basis it can be concluded that most of the manganese and cobalt are in a four-fold coordination state, as a result of which they are incorporated into the structural network of the glass and, in consequence, the CLTE decreases and the microhardness increases.

The amount of harmful substances released from the glazes was determined by analyzing extracts. Samples of glazed ceramic dishware were filled with a 4% solution of acetic acid, simulating the acids present in food. The exposure in this experiment lasted for $24 h \pm 10 min$. It was determined that the extracts from the glassy coatings satisfied the hygienic requirements with respect to all organoleptic indicators. They were all colorless and transparent. The exterior appearance of the coatings did not change. The migration values for the harmful substances released in the acetic-acid extracts are presented in Table 1.

² Here and below — weight content.



Analysis of the amount of boron ions released from the chromium containing glazes into the 4% acetic acid solution (see Fig. 1) shows that as the chromium oxide content increases, the boron ion concentrations increase and are 0.6 and 0.9 mg/liter for the compositions obtained with colored frits (A1, A5) and 1.2 and 7.7 mg/liter for compositions where chromium oxide was added to transparent frit (A1f, A5f). As for the migration of aluminum ions, it too increases when an oxide colorant is added — for the compositions A1 and A5 the migration of aluminum ions is 1.5 times greater than for the compositions where Cr_2O_3 was added to the frit.

The concentrations of chromium ions released from the experimental compositions are 9.5 and 12.0 mg/liter for A1f and A5f and 8.0 and 10.5 mg/liter for A1 and A5, which on average is 100 times higher than the admissible amounts of migration. Such a high level of migration is evidently explained by the fact that chromium oxide is a surface-active substance [4], it is not incorporated into the structural network of the glass, and it occupies only free voids in the glass, out of which it is easily washed. According to S. G. Kovchur's data [5], chromium does not form any compounds with silica and essentially does not mix with silica in the

TABLE 1.[illegible]

melt. The solubility of chromium in silicate glasses is, as a rule, negligible.

An iridescent film forms on copper-containing glazes. Scientists regard this film as the first stage of crystallization [6]. This is probably why negligible copper-ion migration, equal to 0.01–0.03 mg/liter, is observed in glazes containing copper (see Fig. 1b).

Analysis of the migration of boron ions released into a 4% solution of acetic acid shows that as the copper oxide content increases from 1 to 8% the migration of boron ions also increases. In addition, three time more B^{3+} ions migrate from coatings based on colored frits (B1f and B8f) than from compositions (B1 and B8) based on transparent frit. As for the migration of aluminum ions, for the compositions B1f and B8f it remains essentially constant — 0.2 mg/liter and increases by a factor of 4.5 for composition B8.

The glazes containing manganese oxide become covered with an opalescent film, which evidently forms as a result of oxygen becoming embedded in the surface of the glaze during heat treatment [6]. As a result, a film with a nonstoichiometric composition appears on the surface. This is probably the explanation for the negligible migration of manganese ions into the acetic-acid extracts. An increase in the migration of boron and aluminum ions with increasing Mn_2O_3 content is also observed for compositions containing manganese (see Fig. 1c).

This is especially clearly seen for compositions where this oxide was introduced directly into the batch. For example, increasing the manganese oxide content from 1 to 8% increases the migration of boron and aluminum ions by a factor of 25 on average. For compositions where Mn_2O_3 was introduced into the frit (C1f and C8f), the boron- and aluminum-ion migration doubles on average when oxide colorant is introduced, equaling 0.05 and 0.1 mg/liter for boron and 0.2 and 0.5 mg/liter for aluminum. Manganese oxide added to frit is probably in a four-fold coordination state. This allows it to become incorporated into the aluminoborosilicate framework of the glass, thereby increasing polymerization and therefore decreasing migration.

Analyzing the boron and aluminum amounts released from cobalt-containing glazes (see Fig. 1d) shows that as the cobalt oxide content increases from 1 to 6% the migration of boron and aluminum ions increases by a factor of 2–2.5 on average for compositions based on colored frits (D1, D6). The migration of the indicated substances for coatings based on transparent frits (D1f, D6f) remains essentially constant and equals 0.1 mg/liter (boron) and 0.2 mg/liter (aluminum). The concentration of the cobalt released from compositions is 2–12 times higher than the admissible amounts and equals, respectively, 0.27 and 1.2 mg/liter for the D1f and D6f compositions and 0.18 and 0.92 mg/liter for the D1 and D6 compositions.

The data obtained suggest that for all compositions increasing the content of an oxide colorant results in disorder-

ing of the aluminoborosilicate framework and facilitates washing of boron and aluminum ions out of it.

Infrared spectra were obtained with a Nexus spectrophotometer manufactured by the Nicolet Company (USA). The samples were prepared by pressing a mixture of powdered KBr and the experimental substance (300 : 1).

The presence of absorption bands at 1400, 1066–1093, 80, 700, and 465 cm^{-1} can be seen in the spectra of the initial glasses. The main absorption band is observed at 1066–1093 cm^{-1} , which suggests the presence of regions with essentially unbroken Si–O–Si bonds. The small shift of the maximum of the main band into the low-frequency region in the glass spectra could be due to isomorphic substitution of aluminum ions for some silicon ions in the silicon–oxygen tetrahedra. The atomic vibrations in the Si–O–Si bonds also correspond to the absorption bands at 680–720 and 400–500 cm^{-1} . The absorption band at 800 cm^{-1} indicates that six-member rings of $[SiO_4]$ tetrahedra could be present in the glass framework [7]. The absorption bands peaking at 720, 790, and 810 cm^{-1} could be due to the splitting of triply degenerate atomic vibrations in $[AlO_4]$ groups.

Absorption bands at 577–630 cm^{-1} appear in the IR spectra of chromium-containing glazes as the chromium oxide content increases from 1 to 5%. This suggests that chromium oxide participates in the rupture of the silicate network with Si–O bonds being formed. This is probably why boron-, aluminum-, and chromium-ion migration increases in this composition as the chromium oxide content increases.

The IR spectra of manganese- and copper-containing glasses are essentially independent of the amounts of Mn_2O_3 and CuO. As the content of manganese and copper oxides increases, only a broadening of the lines in the spectrum occurs, indicating that the degree of disordering of the structure of these glasses increases as compared with the matrix.

The dependence of the IR spectra of the glazes on the CoO concentration makes it possible to evaluate the change in the glass structure as more and more CoO is added as carefully as. When the CoO content is negligible (1%), the IR spectrum is essentially identical to that of the initial matrix, indicating that their structures are similar. The addition of 6% CoO into the batch (composition D6) probably results in the appearance of quite extended cluster-type cobalt–oxygen formations, which have a weaker effect on the borate network [8]. These cluster structures bind oxygen from sodium oxide, impeding the formation of four-fold coordinated boron, and form complexes of the type $Na^+[CoO_{4/2}]^-$. The more cobalt oxide is introduced into the glass, the more boron is in the three-fold coordinated state, as a result of which it is more easily washed out in the acetic acid extract. As for aluminum, evidently, an oxygen deficit prevents aluminum from switching into the four-fold coordinated state. This is probably the explanation for the increase of aluminum-ion migration as the cobalt oxide content increases from 1 to 6%.

The spectrum of the glass D6f differs from that of the glass D6. The intensity of the band at 1400 cm^{-1} increases (the vibrations of the B–O bonds in groups with three-fold

coordinated boron), the shoulder at 1280 cm^{-1} practically vanishes (the stretching vibrations of the $\text{B}^{3+}-\text{O}-\text{B}^{3+}$ bridge bonds), the band centered at 1080 cm^{-1} (corresponding to the structural groups $[\text{SiO}_4]$) becomes narrower, and the intensity of the band centered at 700 cm^{-1} increases somewhat. Lines appear at 614 cm^{-1} (vibrations of the product formed when the silicate network ruptures) and 780 cm^{-1} , which corresponds to combinations of six-member borate rings. Apparently, the formation of these structures can be explained by cobalt oxide becoming embedded in the borate network. This is probably the reason for the decrease in the boron-ion migration.

According to published data [8], cobalt-containing borosilicate glasses are characterized by the presence of absorption bands, due to $\text{Co}-\text{O}$ bonds, in the range $450-650\text{ cm}^{-1}$ in the IR spectra. We were not able to observe in the spectra of our experimental cobalt-containing glazes any bands which could be unequivocally attributed to these bonds. Probably, they occur in the spectral regions where strong bands due to vibrations of silicon- and boron-oxygen groups lie ($400-550$ and $650-750\text{ cm}^{-1}$) and are not distinguishable against this background. The CoO -induced changes in the structure of the glasses can be judged only indirectly on the basis of the changes in the position and intensity of the bands of the main structural groups.

In summary, data have been obtained on the migration of harmful substances from colored glazes into a model medium simulating food products. It was determined that the colored glazes obtained by adding Cr_2O_3 , CuO , CoO , and Mn_2O_3 in the amounts studied in the present work are characterized by elevated migration of boron and aluminum ions compared with a transparent base. As the content of oxide colorants in the colored glazes increases, the amount of

harmful substances released, normalized to the sanitary norms, increases. The migration of harmful substances from compositions tends to decrease when oxide colorants are added to the batch. Large quantities of chromium ions are released from the glazes into the model media. The concentrations are 80–120 times higher than the admissible values. The migration of harmful substances into acetic acid extract does not exceed the maximum admissible concentrations only in compositions containing 1% copper and manganese oxides (B1, C1, and C1f). This permits their use as glazes for articles which come into contact with food.

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